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IODINE

By Phyllis A. Lyday

1989

U.S. DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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IODINE

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COVER PHOTO:
George D. Nelson, mission specialist, aboard the space shuttle Discovery performing zero gravity experiments to produce lead iodide crystals. More details under current research. (Photo is courtesy of NASA.)

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IODINE

By Phyllis A. Lyday

Mrs. Lyday, a physical scientist with the Bureau of Mines, has been the commodity specialist for iodine for 11 years. Domestic survey data were prepared by Blanche Hughes, mineral data assistant, and international data tables were prepared by Peter Roetzel, international data assistant.

Three producers of crude iodine supplied approximately one-half of domestic demand; the remainder was imported. Because some exports and imports are in product categories rather than crude products, net imports are not clearly developed. The major world producer, Japan, produced iodine from brines associated with gas production. The second largest producer, Chile, produced iodine as a coproduct of sodium nitrate.

DOMESTIC DATA COVERAGE

Domestic production data for iodine are developed by the Bureau of Mines from a voluntary survey of U.S. operations. Of the four operations to which a survey request was sent, three responded, representing an estimated 55% of the total production shown in table 5.

LEGISLATION AND GOVERNMENT PROGRAMS

The Food and Drug Administration extended the provisional listing for Red Dye No. 3, erythrosine containing 58% iodine by weight, until January 29, 1990, for cosmetic uses.[1]

STRATEGIC CONSIDERATIONS

The National Defense Stockpile (NDS) contained 6.1 million pounds of crude iodine valued at $54 million in inventory at yearend. The stockpile goal remained at 2.6 million kilograms (kg) (5.8 million pounds). Responsibility for the NDS was transferred from the Federal Emergency Management Agency and the General Services Administration to the Department of Defense (DOD) (Public Law 100–180). Within DOD, the Defense Logistics Agency (DLA) was to handle the buying, selling, and storing of NDS materials. Executive Order 12626 designated the Secretary of Defense as the National Defense Stockpile Manager.

The National Defense Authorization Act of 1989 (Public Law 100–456) authorized the stockpile manager to dispose of 19 materials, including iodine, determined to be in excess of stockpile requirements. DLA announced that offers for the purchase of iodine would be considered during fiscal year 1989. At yearend 1988, 200,000 pounds was disposed of, leaving 137,657 kgs (303,482 pounds) in excess of the goal at yearend 1989 that was valued at $2.4 million or $17.24 per kg ($7.82 per pound).

PRODUCTION

IoChem Corp., located 2 miles east of Vici, OK, produced iodine by the blowing-out process. IoChem expanded capacity from about 1 million pounds per year to about 4 million pounds per year. North American Brine Resources operated two miniplants at Dover and Hennessey in Kingfisher County, OK. The plants were at oil field reinjection disposal sites where iodine concentrations ranged up to 1,200 parts per million (ppm). The company completed a new $5 million plant in Harper County. Woodward Iodine Corp., a subsidiary of Asahi Glass Co. of Japan, produced iodine from brines using the blowing-out process.

CONSUMPTION AND USES

Iodine was used in animal feed supplements, catalysts, inks and colorants, pharmaceutics, photographic equipment, sanitary and industrial disinfectants, stabilizers, and radiopaque medium. Other uses included production of high-purity metals, motor fuels, iodized salt, and lubricants.

A major use of iodine is as a catalyst in the production of acetic acid by the Monsanto process. BP Chemicals Inc. modified the process to coproduce acetic acid and acetic anhydride. BP is the second largest acetic acid producer with a capacity of 870,000 tons.[2]

Uniroyal Chemical Inc. is a major consumer of iodine for use as an oxidizer in the production of rubber chemicals and elastomers with joint ventures in Brazil, India, Korea, and Mexico. Uniroyal Chemical Co. was purchased with $240 million cash and $560 million as assumed debt in a leverage buyout by a management led team.[3]

Ecolab Inc., a major consumer of iodine for use in cleaning products, sold Henkel KGaA, its West German counterpart, an 11.8% voting interest in preferred stock for $110 million.[4]

GAF Corp. is a major consumer of pyrrolidone-base chemicals that can be used as an environmentally safe cleaning solvent replacing chlorofluorocarbons.[5]

Eastman Kodak Co., a major consumer of iodine in photographic uses, formed a new business unit, Eastman Fine Chemicals, that included Sterling Organic external chemical sales business and sections of Eastman Chemicals specialty organic operations.[6]

Mallinckrodt Inc., a subsidiary of International Minerals & Chemical Corp., began marketing a nonionic contrast medium for radiology and cardiology X-ray procedures. The United States market for X-ray contrast media

is about $500 million annually. The worldwide market was more than twice the U.S. market.[7]

Ceralure, an iodine-containing lure for the Mediterranean fruit flies, developed by the U.S. Department of Agriculture, may replace the use of helicopter sprays.[8]

PRICES

The average declared c.i.f. value for imported crude iodine was $17.68 per kg ($8.05 per pound). The average declared c.i.f. value for imported crude iodine from Japan averaged $17.64 per kg ($8.00 per pound). The average declared c.i.f. value for iodine imported from Chile was $18.01 per kg ($8.17 per pound.

Quoted yearend U.S. prices for iodine and its primary compounds are shown in table 2.

FOREIGN TRADE

The U.S. Government adopted the Harmonized Commodity Description and Coding System (Harmonized System) as the basis for its export and import tariff and statistical classification systems. The system is intended for multinational use as a basis for classifying commodities in international trade for tariff, statistical, and transportation purposes. The Harmonized System as proposed includes resublimed and crude iodine under the same code, and the duty rate is free.

WORLD REVIEW

The World Health Organization, headquartered in Geneva, Switzerland, published "Guidelines for Iodine Prophylaxis following Nuclear Accidents" (EH-35). The guidelines were a result of experience gained from the Chernobyl nuclear accident that exposed population groups to radioactive iodine.

Capacity

The data in table 4 are rated capacity for plants as of December 31, 1989. Rated capacity is defined as the maximum quantity of product that can be produced in a period of time on a normally sustainable long-term operating rate, based on the physical equipment of the plant, and given acceptable routine operating procedures involving labor, energy, materials, and maintenance. Capacity includes both operating plants and plants temporarily closed that in the judgment of the author can be brought into production within a short period of time with minimum capital expenditure.

Mine capacity for iodine is based on rated capacity as reported by the company, by another government agency, or another published source.

TABLE 1

U.S. CONSUMPTION OF CRUDE IODINE, BY PRODUCT

Product	1988		1989	
	Number of plants	Consumption (thousand kilograms)	Number of plants	Consumption (thousand kilograms)
Reported consumption:				
Resublimed iodine	7	86	7	143
Hydriodic acid	4	42	3	49
Calcium iodate	(1)	(1)	(2)	(2)
Calcium iodide	(1)	(1)	3	119
Cuprous iodide	(1)	(1)	3	15
Potassium iodide	7	886	6	829
Potassium iodate	(1)	(1)	5	56
Sodium iodide	5	177	4	46
Other inorganic compounds	13	1,027	14	821
Ethylenediamine dihydroiodide	5	390	4	398
Other organic compounds	10	245	8	426
Total	[3]29	2,853	[3]31	2,902
Apparent consumption	XX	4.3	XX	4.8

XX Not applicable

[1] Included in "Other organic compounds."

[2] Included with calcium iodide for 1989.

[3] Nonadditive total because some plants produce more than one product.

TABLE 2

YEAREND 1989 PUBLISHED PRICES OF ELEMENTAL IODINE AND SELECTED COMPOUNDS

	Dollars per kilogram [1]	Dollars per pound [1]
Calcium iodate, FCC drums, f.o.b. works	$16.42	$7.44
Calcium iodide, 50-kilogram drums, f.o.b. works	23.65- 25.65	12.07- 11.62
Iodine, crude, drums	19.00- 20.00	8.61- 9.06
Iodoform, N.F., 300-pound drums, f.o.b. works	24.00	10.82
Potassium iodide, U.S.P., drums, 5,000-pound lots, delivered	9.15	4.14
Iodine, U.S.P.	17.00	7.70
Sodium iodide, U.S.P., crystals, 5,000-pound lots drums, freight equalized	10.15	4.60

[1] Conditions of final preparation, transportation, quantities, and qualities not stated are subject to negotiations and/or somewhat different price quotations.

Source: Chemical Marketing Reporter. V. 237, No. 1, Dec. 29, 1989, pp. 32-39.

Chile

Sociedad Química y Minera de Chile (SOQUIMICH) was the largest producer of iodine in Chile. The María Elena and Pedro de Valdivia plants produced iodine, sodium nitrate, potassium nitrate, and sodium sulfate. SOQUIMICH continued to operate a plant at Puelma. SOQUIMICH had a joint venture with Israel Chemicals

TABLE 3

U.S. IMPORTS FOR CONSUMPTION OF CRUDE IODINE, BY TYPE AND COUNTRY

(Thousand kilograms and thousand dollars)

Country	1988		1989	
	Quantity	Value[1]	Quantity	Value[1]
Iodine, crude:				
Belgium	11	256	30	545
Canada	(2)	5	(2)	9
Chile	792	13,828	1,014	18,298
Germany, Federal Republic of	—	—	(2)	1
Japan	450	7,812	2,251	39,751
Mexico	—	—	13	178
Sweden	—	—	(2)	13
United Kingdom	2	43	—	—
Total	[3]1,255	21,944	3,309	58,795
Iodide, potassium:				
Germany, Federal Republic of	(2)	6	1	28
India	28	478	7	121
Italy	3	11	9	31
Japan	(2)	10	—	—
Sweden	(2)	3	—	—
Switzerland	—	—	(2)	5
United Kingdom	2	138	—	—
Total	[3]34	646	17	185
Iodine, resublimed:				
Canada	(2)	2	NA	NA
Finland	(2)	3	NA	NA
Germany, Federal Republic of	(2)	1	NA	NA
Japan	1,969	33,326	NA	NA
Total	[3]1,969	33,332	NA	NA
Grand total	3,258	55,912	3,326	58,980

NA Not available because a change in reporting format; crude and resublimed iodine are now one category.
[1] Declared c.i.f. valuation.
[2] Less than 1/2 unit.
[3] Data may not add to totals shown because of independent rounding.

Source: Bureau of the Census.

Ltd. named Compania Quimica Internacional de Desarrollo (IDC Co.) dedicated to research and development in the inorganic chemicals and fertilizers.[9]

North Lily Mining Co. of the United States formed a joint venture, named Taltal Joint Venture, with Zurfund International Ltd., Canada, to mine iodine. North Lily will operate the deposit known as the Yolanda Project through Minera Northern Resources, a wholly owned subsidiary. Davey McKee Corp. was retained by the Taltal Joint Venture to undertake a feasibility study of the Yolanda Project.[10]

Other companies active in iodine production in Chile included Amsterdam Chemical Pharmaceutical Minera (ACF Minera), a joint venture of the Sociedad Contractual Minera Lagunas and the Amsterdam Pharmaceutical Co. of the Netherlands. ACF Minera was operating a plant originally built by Minera Lagunas. The plant had been expanded with a $3 million investment. The crude product was shipped to the Netherlands for use by the producing company rather than for an open market.[11] Cia Minera Chilbras, a Chilean-Brazilian joint venture, produced iodine from nitrate deposits in the Salar de Bellavista.[12] The Merck Pharmaceutical Co. of the Federal Republic of Germany was involved in a project to produce between 4 to 5 tons per year of iodine from nitrate tailings near Huara in the Iquiqui region.[13] Compania Minera Sierras de Tarapaca began production of iodine at the San Pedro plant 37 kilometers east of Pozo Almonte, Tarapaca. The plant cost $2 million and had a 360 tons per year of capacity.[14] Banco Bilbao Vizcaya S.A., Spain, announced a $19.2 million iodine recovery facility to be built on 1,184 hectares of land purchased for $14 million from Cia Minera Gran Tamarugal S.A. The plant planned to produce 4,750 tons of iodine the first 10 years with production destined for markets in Europe.[15] Compania Minera del Alba operated a small plant at Salar de Lagunas.

Indonesia

The only producer of crude iodine was the state-owned pharmaceutical firm, P. T. Kimia Farma, that operated a plant at Watudakon near Mojokerto, East Java.

Japan

Production of iodine was from underground brines associated with natural gas. Japan was the world's leading producer of iodine in 1989. Six companies operated 17 plants with a total production capacity of 20 million pounds per year.

United Kingdom

Thornton Processing Ltd., Bradford, reported that during 1988 more

TABLE 4

WORLD IODINE ANNUAL PRODUCTION CAPACITY,[1] DECEMBER 31, 1989 RATED CAPACITY[2]

(Thousand kilograms)

Country	Capacity
North America: United States	1,200
South America: Chile	3,800
Europe: U.S.S.R.	2,000
Asia:	
China	500
Indonesia	4
Japan	7,000
Total	7,600
World total	[3]15,000

[1] Actual capacity limited by brine supply.
[2] Includes capacity at operating plants as well as at plants on standby basis.
[3] Data do not add total shown because of independent rounding.

than $2 million worth of iodine was recovered at the Caledonia plant from industrial residues, principally those generated from growing sodium iodide crystals.

CURRENT RESEARCH

Because of their reaction with metals in the presence of water, alkyl halides may find use in metal recovery and refining and methyl iodide in metallurgical processing. Because algae serve as a major source of environmentally occurring methyl iodide, a microorganism approach in the metallurgical process could be possible in the future.[16]

When natural rubber, a polymer, is treated with iodine, it becomes 10 orders of magnitude more highly conducting than native rubber. If further research can improve the conductivity, then commercial applications could be possible.[17]

A researcher with Nippon Steel Corp., Japan, used a catalyst of cadmium and cesium iodides to make liquid crystalline polyesters that could be used in magnetic recording tapes, dielectrics in capacitors, and thermal printer ribbons.[18]

Three experiments to grow lead iodine crystals were completed during a National Aeronautics and Space Administration's *Discovery* space shuttle flight of September 1988. Lead iodide crystals are used as image intensifiers for X-ray and gamma-ray films. Larger crystals would produce better films. Crystals grown in space are superior to Earth-grown crystals for some applications.[19]

OUTLOOK

Iodine production capacity in the United States and Chile has doubled during the past decade, ensuring an adequate world supply. Uses for iodine in specialty chemicals has remained stable. New processes have decreased the amount of iodine while demand has increased. For example, a patent was obtained that required less iodine to provide the same sanitizing ability.

BACKGROUND

Definitions, Grades, and Specifications

Commercial crude iodine normally has a minimum purity of 99.5%. Resublimed iodine is usually 99.9% purity. Most iodine is converted for industrial use to potassium iodide, sodium iodide, and other inorganic compounds, as well as numerous organic compounds.[20]

Geology-Resources

Iodine occurs in rocks and soils, surface and underground brines, and in caliche ores. Michigan brines contain about 30 parts per million (ppm) of iodine in the Sylvania Formation of Devonian age. California brines contain 30 to 70 ppm of iodine in brines associated with oilfields in the middle Miocene age, Monterey Formation, and the lower Pliocene age Repetto Formation. Louisiana brines contain about 35 ppm of iodine. In Oklahoma, iodine concentrations associated with oil and gas range between 150 to 1,200 ppm. In Woodward County, OK, the iodine occurs in the Morrowan Formation of Pennsylvania age.

Extensive iodine-bearing nitrate ores occur in caliche deposits in a belt several hundred kilometers long in the Atacama Desert of northern Chile. The ore layers are 1 to 3 meters thick, usually flat or gently dipping and near the surface. Evaporate minerals such as lautarite (CaI_2O_6) and dietzeite ($2CaO{\cdot}I_2O_5{\cdot}CrO_3$) occur as cementing material in unconsolidated surface material or as veins and impregnations in bedrock.

Japanese brines contain 50 to 135 ppm of iodine in the Kiwada, Otadai, and Umegase Formations of the Kazusa Group of Pliocene age. The major iodine-producing area was the southern Kanto Gasfield, which extends over Chiba, Tokyo, and Kanagawa Prefectures. Iodine was produced in the Niigata and Nakojo Gasfields in Niigata Prefecture, on the Sea of Japan side of central Japan, and the Sadowara Gasfield in Miyazaki Prefecture, southern Kyushu.

In Indonesia, iodine occurs with trace amounts of bromine in brines associated with oil. The most important iodine-producing area is the Gujangon anticline of sandstone and diatomaceous marls of the Upper Pliocene, Kailiberg Formation.

TABLE 5

CRUDE IODINE: WORLD PRODUCTION, BY COUNTRY[1]

(Kilograms)

Country[2]	1985	1986	1987	1988[p]	1989[e]
Chile	3,020,000	3,076,000	3,115.000	4,035,000	4,000,000
China[e]	500,000	500,000	500,000	500,000	500,000
Indonesia	13,000	6,000	8,000	10,000	[3]14,000
Japan	7,251,000	7,389,000	7,014,000	7,451,000	7,600,000
U.S.S.R.[e]	2,000,000	2,000,000	2,000,000	2,000,000	2,000,000
United States	W	W	W	998,000	[3]1,508,000
Total	[4]12,784,000	[4]12,971,000	[4]12,637,000	14,994,000	15,622,000

[e] Estimated. [p] Preliminary. W Withheld to avoid disclosing company proprietary data.

[1] Table includes data available through May 30, 1990.

[2] In addition to the countries listed, New Zealand also produces elemental iodine, but data are not available and available information is inadequate for formulation of reliable estimates of output levels.

[3] Reported figure.

[4] Excludes U.S. production.

On Okinawa, iodine occurs in concentrations of about 85 ppm in the Tomigusuku Formation of the Shimajiri Group of late Miocene-early Pleistocene age.

Technology

In the United States and Japan, iodine is removed from brines by processes that separate the brines from any associated oil or gas. In the blowing-out process, brine is acidified and iodine is liberated by reducing the pH to about 3. A countercurrent stream of air transports the liberated iodine to a second tower in which the iodine is absorbed by a solution of hydriodic acid. The iodine settles, is filtered, and melted under concentrated acid. Brine stripped of iodine is treated and then reinjected into its subsurface formation of origin.

In the absorption process, brine is passed through an absorber and the waste brine is neutralized and sent to a disposal well. The absorbent laden with iodine is treated with an alkaline solution to regenerate the absorbent and eludes iodine as sodium iodide. Iodide is precipitated under acid.

Japanese plants also use an ion-exchange resin. Upon saturation, the iodine is eluted using a caustic solution that regenerates the resin. Iodine is then processed with a sodium chloride solution and melted under acid.

Chilean caliche deposits are mined by open pit methods. The ore is leached with an alkaline solution to dissolve the iodine as sodium iodate, which is converted to sodium iodide. Iodine is precipitated by reacting with additional alkaline solution. The precipitated iodine is filtered in bag filters and the iodine free-leach solution is returned to the nitrate-leaching cycle.

Economic Factors

Prices.—Changes in the official price of crude iodine have in the past been initiated during shortages. Because iodine cannot be substituted in radiopaque, animal feeds, catalysts, and stabilizers readily, shortages tend to cause the accumulation of inventories. An adequate supply tends to stabilize the price.

Costs.—Electrical costs for maintaining the pumps to bring the brine to the surface, for air-blowing the iodine, and for reinjecting the brine are major components of maintenance costs. Capital costs have been estimated at $20 per pound of annual iodine production. These costs include high-quality stainless steels because iodine is highly corrosive. In addition, the brine must be leased from private landowners over large acreage for many years. The principal material cost is for chlorine because 1 pound is required for every 1.4 to 1.8 pounds of iodine produced.

Taxes.—Crude and resublimed iodine enter the United States duty free. Calcium and cuprous iodine has a 25% ad valorem for non-most-favored-nation status. Potassium iodide has a 2.8% ad valorem for most-favored-nation status and 7.5% ad valorem for non-most-favored-nation status.

Depletion Provisions.—The domestic and foreign depletion allowances for iodine are 14% of gross income, and they may not exceed 50% of net income without the depletion deduction.

Operating Factors

Environmental Requirements.—The reinjection of waste brine is a limiting factor to the production of iodine. During 1982, the Environmental Protection Agency (EPA) reclassified disposal wells for spent brine after halogen extraction as Class 5 wells. All of the reinjection wells for iodine in Oklahoma were drilled for the reinjection of waste associated with brine production or oil and gas effluent.

Toxicity.—Iodine is absorbed by the body and concentrated in the thyroid. Iodine is essential to higher animals and humans. A normal person requires about 75 mg of iodine per year, which is usually consumed as iodized salt that contains 1 part sodium or potassium iodide to 100,000 parts of sodium chloride. Iodine deficiency is a major cause of goiter.[21]

The maximum safe concentration for short-term air environment exposure of up to 1 hour is 1.0 ppm. Exposure of the lungs and eyes can be irritating at

TABLE 6

TIME-PRICE RELATIONSHIPS FOR CRUDE IODINE

Year	Average annual c.i.f.[1] value, dollars per pound		Average annual c.i.f.[1] value, dollars per kilogram	
	Actual price	Based on constant 1988 dollars	Actual price	Based on constant 1988 dollars
1970	1.15	3.32	5.59	3.32
1971	1.58	4.32	3.48	4.32
1972	1.64	4.28	3.62	4.28
1973	1.72	4.21	3.79	4.21
1974	1.86	4.18	4.10	4.18
1975	2.21	4.52	4.87	4.52
1976	2.13	4.09	4.70	4.09
1977	1.05	3.69	2.31	3.69
1978	2.21	3.71	4.87	3.71
1979	3.37	5.20	7.43	5.20
1980	4.72	6.68	10.41	6.68
1981	6.03	7.78	13.29	7.78
1982	5.97	7.24	13.16	7.24
1983	5.57	6.50	12.28	6.50
1984	4.90	5.50	10.80	5.50
1985	5.38	5.88	11.86	5.88
1986	5.68	6.05	12.52	6.05
1987	6.92	7.15	15.26	7.15
1988	7.92	7.92	17.46	7.92
1989	7.70	7.70	16.98	7.70

[1] Cost, insurance, and freight charges for imported iodine.

Source: Bureau of the Census.

concentrations of 0.1 ppm and should be avoided. Greater exposure can cause severe irritations to the eyes and the respiratory tract and may lead to pulmonary edema.

In 1979 and 1986, nuclear accidents caused the release of radioactive iodine, I^{131}, into the atmosphere. Ingestion of potassium iodide, KI, can reduce the amount of radiation absorbed by the thyroid gland.[22]

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